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Effect of surface modification of indium tin oxide by nanoparticles on the electrochemical determination of tryptophan

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ABSTRACT

The effect of surface modification of indium tin oxide (ITO) by multi wall carbon nanotube (MWNT) and gold nanoparticles attached multi wall carbon nanotube (AuNP-MWNT) has been studied to determine tryptophan, an important and essential amino acid for humans and herbivores. A detailed comparison has been made among the voltammetric response of bare ITO, MWNT/ITO and AuNP-MWNT/ITO in respects of several essential analytical parameters viz. sensitivity, detection limit, peak current and peak potential of tryptophan. The AuNP-MWNT/ITO exhibited a well defined anodic peak at pH 7.2 at a potential of ~669 mV for the oxidation of tryptophan as compared to 760 mV at MWNT/ITO electrode. Under optimum conditions linear calibration curve was obtained over tryptophan concentration range 0.5–90.0 μM in phosphate buffer solution of pH 7.2 with detection limit and sensitivity of 0.025 μM and 0.12 μA μM^{-1}, respectively. The oxidation of tryptophan occurred in a pH dependent, $2e^-$ and $2H^+$ process and the electrode reaction followed adsorption controlled pathway. The method has been found selective and successfully implemented for the determination of tryptophan in human urine and plasma samples using standard addition method. The electrode exhibited an efficient catalytic response with good reproducibility and stability.

1. Introduction

Tryptophan (2-amino-3-(1H-indol-3-yl)-propionic acid), Trp (I) is an important and essential amino acid for humans and herbivores, and is also a potent precursor of several metabolites such as serotonin, melatonin and niacin [1]. It is an indispensable ingredient of various types of proteins, therefore, must be added in human nutrition for establishing and maintaining positive balance of nitrogen. The intake of Trp is necessary as food products and pharmaceutical preparations, since, it is not synthesized in our body [2]. It has been reported that improper metabolism of Trp produces a toxic product in brain which is the possible reason of hallucination, delusions and schizophrenia [3]. Literature survey reveals that Trp is the major constituent of drugs which are used for the treatment of various types of brain related disorders such as depression, schizophrenia and hypertension [3,4]. The distribution of Trp content in human hair has been found to influence the hair pigmentation [5]. Recent reports have indicated that the concentration of Trp present in biological fluids is very low and its altered level causes metabolic disorders, therefore, the rapid and consistent determination of Trp in human body fluids and vegetable food products is of great significance in biochemical research and clinical purposes [6].

Several techniques have been used for the determination of Trp including high performance liquid chromatography [7–10], ion exchange chromatography [11], liquid chromatography with fluorescence detection [12,13], thin layer chromatography with fluorescence detection [14], capillary electrophoresis [15,16], fluorometry [17], chemoluminescence [18–20] and spectrometric techniques [21]. Most of these techniques require heavy and expensive instrumentation along with complicated, tedious and time consuming derivatization, sample preparation and extraction steps. In the last decade electroanalytical techniques have attracted considerable attention for the determination of biomolecules and drugs due to their simplicity, low cost, high sensitivity and rapidness. Several types of modified electrodes have also been used for the determination of Trp including haemin-modified glassy carbon electrode [22], glassy carbon electrode modified with butyrylcholine [2], nafion modified electrode [23], carbon paste electrode incorporating 1-[4-(ferrocenyl ethynyl) phenyl]-1-ethanone (4FEPE) [24] and many more [25–33]. In recent years multi walled carbon nanotubes have attracted generous interest as electrode surface modifier due to their fascinating electronic, chemical and mechanical properties [34]. Further, the fuctionalization of CNTs improved their solubility in biological fluids as well as selectivity of binding to bio-targets of interest [35].

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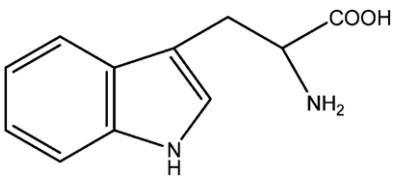

(I)

Scheme 1.

Nanostructure network of nanoparticles have unusual charge/mass transport mechanisms which improved the charge and mass transfer [36]. Gold nanoparticles have been found to enhance the electrode conductivity by facilitating electron transfer thus, improve the electrochemical sensitivity and selectivity [37].

In the present work, effect of surface modification of ITO by the use of multi walled carbon nanotube (MWNT) and gold nanoparticles attached carboxylated multi walled carbon nanotube (AuNP-MWNT) has been studied for the electrochemical oxidation of Trp. A detailed comparison for oxidation of tryptophan has been made for the electrochemical response at bare ITO, MWNT/ITO and AuNP-MWNT/ITO. It is expected that such imperative and fascinating comparison concerning the electro-catalytic activity of the combination of functionalized nanotubes with gold nanoparticles towards the oxidation of tryptophan will provide information about the catalytic activity of MWNT and gold nanoparticles. Good sensitivity, selectivity, reproducibility and stability of AuNP-MWNT/ITO make it attractive for further developments in the field of electrochemical sensors for monitoring similar type of biomolecules in human body fluids as well as in pharmaceutical formulations (Scheme 1).

2. Experimental

2.1. Reagents

Tryptophan was obtained from Loba Chemie, India. Indium tin oxide electrodes spurted glass sheets of size 10 mm × 20 mm × 1.1 mm and resistivity 30 Ω cm^{-2} were obtained from Geomatec, Japan. MWNT (purity > 98%, outer diameter 10–15 nm and inner diameter 2–6 nm) and $HAuCl_4$ were purchased from Aldrich (USA). Ascorbic acid was purchased from Wako pure chemicals industries Ltd., Japan. All solutions were prepared in double distilled water. The urine samples of healthy volunteers were collected from laboratory personnel's and plasma samples were obtained from the Hospital of Indian Institute of Technology Roorkee, Roorkee after getting clearance from the ethics committee of the institute.

2.2. Instrumentation

BAS (Bioanalytical Systems, West Lafayette, USA) CV-50W voltammetric analyzer was used for the voltammetric measurements. The voltammetric experiments were performed using three electrodes single compartment cell equipped with an ITO or MWNT/ITO or AuNP-MWNT/ITO electrode as working, platinum wire as counter and Ag/AgCl (3 M NaCl) as reference electrode. Phosphate buffers solutions (PBS) of pH range 2.4–10.0 (μ = 1.0 M) were prepared according to the reported method [38]. The pH of the buffer solutions was measured using Eutech Instruments pH 510, pH meter after standardization with 0.05 M potassium hydrogen phthalate (pH 4.0 at 25 °C) and 0.01 M borax (pH 9.2 at 25 °C). The optimized square wave voltammetric (SWV) parameters used were: square wave amplitude (E_{sw}): 25 mV; potential step (E): 4 mV; square wave frequency (f): 15 Hz. Cyclic voltammograms were recorded after bubbling high-purity nitrogen for 12–15 min. All potentials reported are with respect to Ag/AgCl (3 M NaCl) at an ambient temperature of 25 ± 2 °C. The surface morphology of the bare and modified ITOs was characterized by recording FE-SEM using Quanta 200-F (FEI Company) FE-SEM instrument.

2.3. Procedures

The gold nanoparticles (AuNP) solution was prepared by reducing Au^{3+} ions to Au^0 with ascorbic acid [39,40]. For this purpose 50 mL of 2.2 mM aqueous ascorbic acid was added to 50 mL of 1.34 mM aqueous $HAuCl_4$ under stirring. The change in solution colour from yellow to deep red indicated the formation of gold nanoparticles which was again confirmed by recording FE-SEM images. In order to make MWNT water soluble, carboxylation was carried out according to the reported method [41].

In order to modify the bare surface of ITO, 100 μL of 1 mg/mL carboxylated MWNT (aq.) was dropped on the clean surface of ITO electrode (10 mm × 10 mm × 1.1 mm) and dried at 60 °C. In the second case, 100 μL solution of the AuNP prepared was dropped on the MWNT layered ITO, followed by drying at 60 °C. The electrodes were prepared by connecting with a thin strip of copper adhesive tape, and then casing with a scotch tape that is made to have a 2 mm-diameter hole on one side. The electrodes were then ready to use for voltammetric experiments. Typical FE-SEM images of the bare and modified ITO electrodes are given in Fig. 1. The deposition of MWNT on ITO surface can be clearly seen as shown in Fig. 1(a). Whereas in Fig. 1(b) white crumb parts observed are gold nanoparticles and, on the backdrop, consistently formed MWNT layer are clearly observed on the surface of ITO. The bare ITO (Fig. 1(c)) simply shows a smooth surface.

3. Results and discussions

3.1. Effect of modification on surface area

The surface area of MWNT/ITO and AuNP-MWNT/ITO was calculated to determine the efficacy of surface modification. For this purpose, cyclic voltammograms were recorded for 1 mM $K_3Fe(CN)_6$ using 0.1 M KCl as the supporting electrolyte at different scan rates. A well defined redox couple was observed at both the electrodes due to the presence of Fe^{3+}/Fe^{2+}. The peak potentials of the redox couples were 265/190 and 237/183 mV at sweep rate of 50 mV s^{-1} using MWNT/ITO and AuNP-MWNT/ITO electrodes, respectively. Thus, the peak separation of anodic and cathodic peaks at AuNP-MWNT/ITO indicates the increased reversibility of the system over MWNT/ITO electrode. There was an enhancement in the peak current values at AuNP-MWNT/ITO electrode in comparison to MWNT/ITO electrode. The surface areas of modified electrodes were found as 0.069 cm^2 and 0.142 cm^2, for MWNT/ITO and AuNP-MWNT/ITO respectively. As the effective surface area of bare ITO electrode was 0.0314 cm^2 the effective surface area of the MWNT/ITO and AuNP-MWNT/ITO increased after surface modification. The effective surface area of AuNP-MWNT/ITO electrode is almost 2 times larger than that of MWNT/ITO and 4 times larger than bare ITO electrode, thereby, indicating that carboxylated MWNTs are helpful towards binding AuNPs on the MWNT layer at ITO surface.

3.2. Comparison of modified ITOs

The electrochemical behaviour of tryptophan was studied by square wave voltammetry using bare ITO, MWNT/ITO and AuNP-MWNT/ITO in order to elucidate the effect of surface modification for Trp determination. Fig. 2 depicts the electrochemical response of 55 μM tryptophan under optimal parameters in phosphate

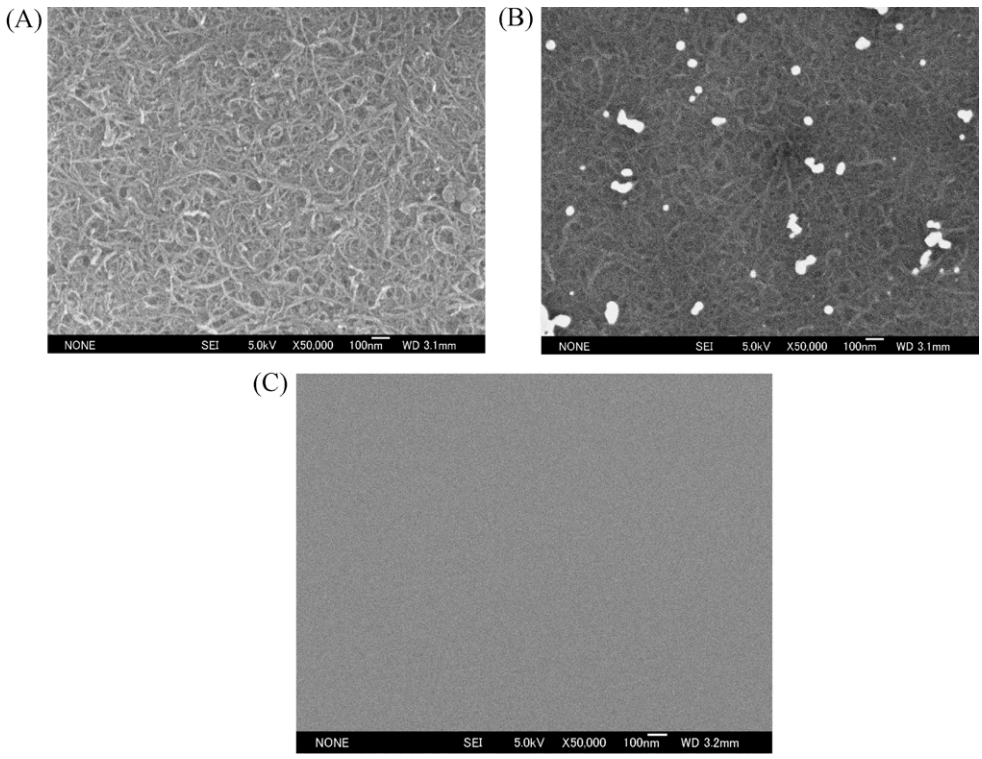

Fig. 1. Typical FE-SEM images observed for (a) MWNT/ITO, (b) AuNP-MWNT/ITO and (c) bare ITO surfaces.

buffer of pH 7.2 using above mentioned three electrodes. A broad bump is observed at bare ITO having peak potential ~870 mV (curve *a*). At MWNT/ITO tryptophan the E_p shifted to ~760 mV (curve *b*), whereas, at AuNP-MWNT/ITO the E_p further shifted to ~669 mV (curve *c*) with enhancement in the peak current. A comparative study clearly indicates that a substantial decrease (~190 mV and ~100 mV) in peak potential of Trp oxidation is observed as compared to bare surface of ITO using AuNP-MWNT and MWNT coatings on ITO, respectively. A significant enhancement in the peak current is also observed for modified electrodes as compared to bare ITO electrode. The shift in peak potential to less positive potential and enhancement in peak current indicate that the composite film containing the combination of carbon nanotubes with gold nanoparticles exhibits efficient electrocatalysis towards Trp oxidation. Hence, AuNP-MWNT/ITO electrode has been used for further detailed studies for tryptophan determination.

3.3. Cyclic voltammetry

Cyclic voltammograms were recorded for blank PBS (pH 7.2) for 55 μM Trp at AuNP-MWNT/ITO electrode as presented in Fig. 3. A well defined single oxidation peak at ~729 mV was obtained using AuNP-MWNT/ITO. The absence of peaks in the reverse scan clearly indicated that the oxidation of tryptophan at this electrochemical sensor is irreversible in nature. To ascertain the nature of the electrode reaction, sweep rate studies were performed in the range 10–1000 mV s^{-1}. The peak current was found to increase with increasing sweep rates and the plot of $i_p/v^{1/2}$ versus log v clearly indicated that the electrode process is adsorption controlled [42,43]. As Trp is found to be oxidised at less positive potentials (~669 mV) with increased peak current using square wave voltammetric technique in comparison to cyclic voltammetry

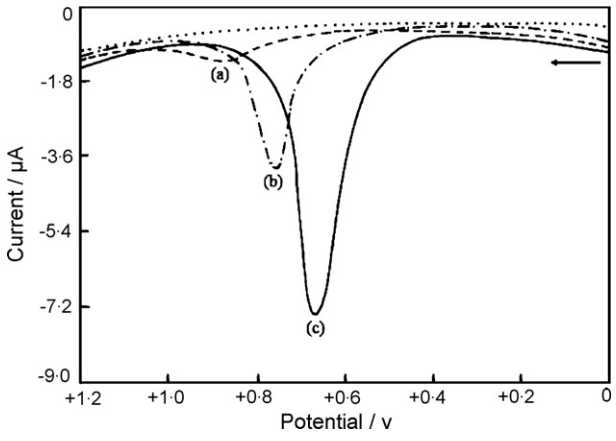

Fig. 2. Cyclic voltammograms obtained for blank PBS (– – –) and 55 μM tryptophan at pH 7.2 using AuNP-MWNT/ITO (—) at 20 mV s^{-1}.

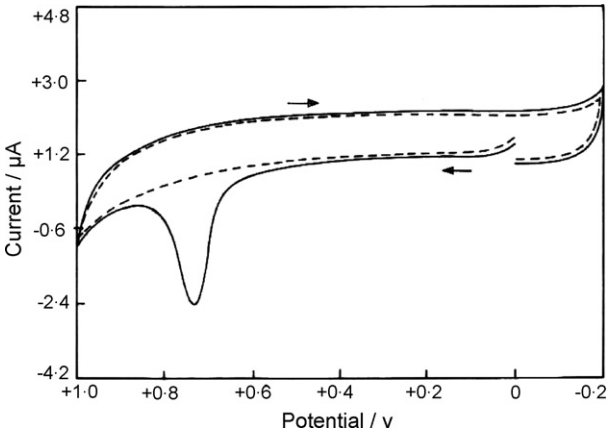

Fig. 3. A comparison of square wave voltammograms of 55 μM Trp using (a) bare ITO (- - -), (b) MWNT/ITO (– – –), (c) AuNP-MWNT/ITO (—) at pH 7.2. The background is shown by (. . .).

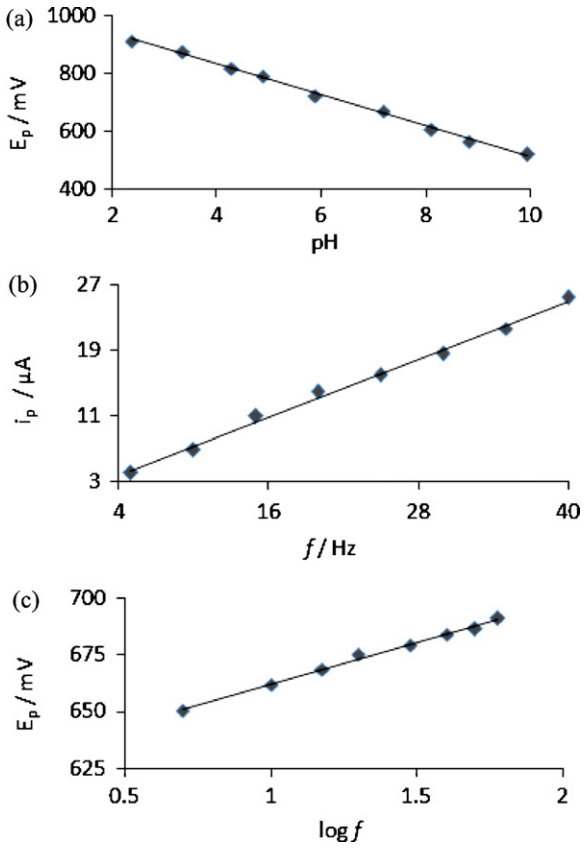

Fig. 4. (a) Dependence of observed peak potential (E_p) on pH, (b) Plot of i_p versus frequency (f) and (c) dependence of E_p on logarithm of square wave frequency (log$f$) for 90 μM Trp using AuNP-MWNT/ITO.

(~729 mV), hence, square wave voltammetry was used for the determination of tryptophan in real samples.

3.4. Electrochemical behavior of tryptophan

The influence of pH on the voltammetric oxidation of 90 μM tryptophan was determined by using square wave voltammetry at AuNP-MWNT/ITO in the pH range of 2.4–10.0. It was observed that peak potential (E_p) of Trp shifted towards less positive potentials with increase in the value of pH as illustrated in Fig. 4(a). The plot obtained between peak potential and pH was linear and the dependence of E_p on pH can be represented by the relation:

$$E_p = [1044 - 53.37 \quad pH] \quad mV \text{ versus } Ag/AgCl$$

having correlation coefficient of 0.997. The value of the slope of E_p versus pH curve was close to 59 mV/pH and indicated that equal number of electrons and protons ($2e^-$ and $2H^+$) were involved in the oxidation of Trp. A similar oxidation reaction of Trp has been reported in the literature [2].

The influence of square wave frequency (f) on peak current and peak potential of tryptophan was examined at pH 7.2 using AuNP-MWNT/ITO. A linear relationship was observed between the oxidation peak current and square wave frequency having correlation coefficient of 0.994 as shown in Fig. 4(b), which indicated adsorption of tryptophan at the electrode surface [44,45]. The dependence of peak current on square wave frequency using AuNP-MWNT film modified ITO can be expressed by the relation:

$$i_p(\mu A) = 0.591 f(Hz) + 1.407$$

having correlation coefficient 0.994. It was found that the peak potential also shifted linearly towards more positive potentials with increase in frequency. The E_p versus log$f$ plot was found to be linear (Fig. 4(c)) and the variation of E_p can be expressed by the equation:

$$E_p(mV) = 36.68 \quad \log \quad f + 625.4$$

having correlation coefficient 0.993. These results are in agreement with the adsorption controlled irreversible electrochemical process [46] and also support the observations obtained from cyclic voltammetric studies.

Table 1
Recovery results obtained for tryptophan in human urine and plasma samples at AuNP-MWNT/ITO.

Spiked (μM)	Urine[a]		Plasma[a]	
	Detected (μM)	Recovery (%)	Detected (μM)	Recovery (%)
Sample 1				
10.00	10.16	101.60	9.86	98.60
30.00	29.85	99.50	30.26	100.87
50.00	49.50	99.00	50.00	100.00
Sample 2				
10.00	10.00	100.00	9.76	97.60
30.00	30.09	100.30	30.16	100.53
50.00	49.92	99.84	51.09	102.18
Sample 3				
10.00	9.76	97.60	9.66	96.60
30.00	30.34	101.13	30.96	103.20
50.00	50.60	101.20	51.64	103.28

[a] The R.S.D value was <2.3% for urine and <1.9% for plasma for $n = 3$.

3.5. Detection limit and sensitivity

Quantitative determination is based on the dependence of peak current on concentration of the compound. To monitor the effect of surface modification of ITO, the variation of oxidation peak current with Trp concentration was studied using bare ITO, MWNT/ITO and AuNP-MWNT/ITO electrodes in order to compare vital analytical parameters including sensitivity and detection limit. Square wave voltammograms representing the systematic increase in oxidation peak current with increase in concentration in the range 0.5–90 μM using AuNP-MWNT/ITO at pH 7.2 are illustrated in Fig. 5. It was found that when the concentration (C) increases the oxidation peak current (i_p) linearly increases at all the three electrodes. The linear calibration curves at all the three electrodes are depicted in Fig. 6.

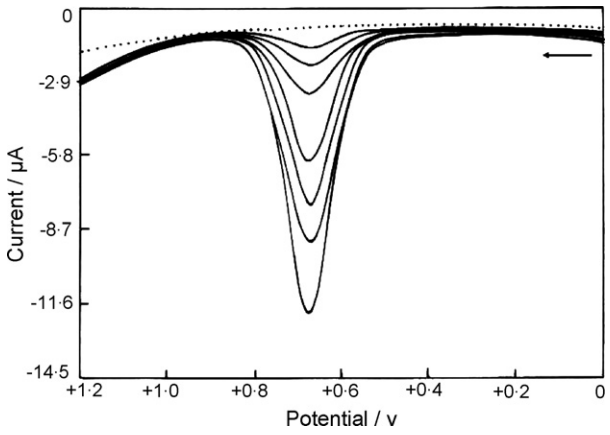

Fig. 5. Observed square wave voltammograms for (i) blank PBS (background) (.....) and (ii) increasing concentration of Trp [curves were recorded at $a = 5$, $b = 10$, $c = 20$, $d = 40$, $e = 55$, $f = 70$ and $g = 90$ μM concentration] using AuNP-MWNT/ITO in PBS of pH 7.2.

Table 2
A comparison of voltammetric response of AuNP-MWNT/ITO with previously reported electrodes for the determination of tryptophan.

Sr. no.	Electrode	Linear range (μM)	Detection limit (μM)	Ref. no.
1	GCE/Nafion/TiO_2	5–140	0.70	[25]
2	GNP/CILE	5–900	4.0	[26]
3	PGA/CNTPE	0.05–100	0.01	[27]
4	Macrocyclic/CPE	1.96–1000	0.098	[28]
5	CILE	8.0–1000	4.80	[29]
6	CNF-CPE	0.10–119	0.10	[30]
7	Au-NPs/GCE	0.09–50	0.08	[31]
8	AuNP/CNT/GCE	0.03–2.5	0.010	[32]
9	4-ABA/GCE	1.0–100	0.20	[33]
10	AuNP-MWNT/ITO	0.5–90.0	0.025	Proposed method

CPE – carbon paste electrode, CILE – carbon ionic liquid electrode.

Linear dependence of peak current (after subtracting background current) on concentration can be expressed by the equations:

$$i_p(\mu A) = 0.119\ \ C\,(\mu M) + 0.268\ \ \text{at AuNP} - \text{MWNT/ITO}$$

$$i_p(\mu A) = 0.058\ \ C\,(\mu M) + 0.089\ \ \text{at MWNT/ITO}$$

$$i_p(\mu A) = 0.005\ \ C\ \ (\mu M) + 0.003\text{at bare ITO}$$

having correlation coefficients 0.998, 0.998 and 0.997, respectively. The detection limit was calculated by using the relation $3\sigma/b$, where σ is standard deviation of blank and b is slope of the calibration curve and found to be 0.025 μM, 0.054 μM and 0.30 μM for AuNP-MWNT/ITO, MWNT/ITO and bare ITO, respectively. Thus, it can be seen that surface modification of ITO by MWNT and AuNP-MWNT lowered the detection limit by ~6 times and ~12 times as compared to bare ITO. The observed sensitivities at AuNP-MWNT/ITO, MWNT/ITO and bare ITO are 0.12 $\mu A\,\mu M^{-1}$, 0.06 $\mu A\,\mu M^{-1}$ and 0.005 $\mu A\,\mu M^{-1}$, respectively. Therefore, it can be concluded that addition of AuNP to MWNT/ITO further enhance the oxidation of tryptophan in terms of imperative analytical parameters such as detection limit, sensitivity, peak potential and current. The robustness of the method was examined by the consistency of peak height and peak shape with the deliberately small changes in the experimental parameter such as square wave frequency, square wave amplitude and pH. It is a measure of its capacity to retain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage. These parameters were deliberately changed one at a time and the effect of these changes on the assay studies was carried out. It was found that such a variation did not cause change in peak current and peak shape and hence, the proposed procedure was considered robust. Owing to comparatively better electroanalytical performance at AuNP-MWNT/ITO it is decided to use this electrode for electroanalysis of tryptophan in biological samples.

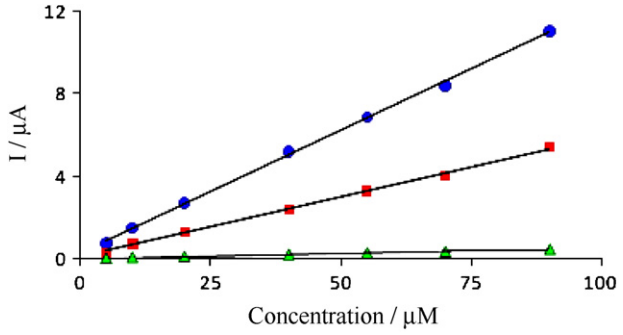

Fig. 6. Calibration plots observed for Trp using bare ITO (▲), MWNT/ITO (■) and AuNP-MWNT/ITO (●) at pH 7.2.

3.6. Real sample analysis using AuNP-MWNT/ITO

In order to establish the analytical utility of the proposed sensor, attempts have been made to determine tryptophan in urine and blood plasma samples by using standard addition method. Blood plasma samples were ultra centrifuged at a speed of 1000 rpm for 5 min and supernatant blood plasma was used for the determination of tryptophan. Urine and blood samples were diluted 2 and 4 times, respectively with phosphate buffer solution of pH 7.2 prior to analysis. Three human plasma and urine samples obtained from healthy volunteers were spiked with known amounts of standard Trp ranging from 10 to 50 μM, followed by recording their square wave voltammograms. In all the cases well-defined peak was observed with $E_p \sim 669$ mV corresponding to the oxidation of tryptophan. The concentration of Trp was calculated using calibration plot for AuNP-MWNT/ITO and the results observed are listed in Table 1. The recoveries varied in the range from 97.6% to 101.6% in the case of urine and from 96.6% to 103.3% in the case of plasma. The recovery data lie in the acceptable range and hence the proposed sensor can be utilized successfully for the determination of Trp in human body fluids with adequate accuracy.

3.7. Stability and reproducibility of electrode

The stability of AuNP-MWNT/ITO electrode was evaluated by measuring the voltammetric current response of constant tryptophan concentration (20 μM) over a period of 8 days. The electrode was used day by day and stored in air at room temperature. It was observed that during first 5 days the current response had almost remain unchanged and in the next 3 days the current sensitivity decreased about 2.62% of its initial value. These results suggest that the modified electrode possesses adequate stability for Trp determination. To characterize the reproducibility of AuNP-MWNT/ITO electrode, successive voltammetric measurements of 20 μM Trp were carried out at pH 7.2. The results of eight repetitive measurements showed relative standard deviation (R.S.D.) of 1.96% and 2.19% for intra-day and inter-day precision, respectively, which confirmed the excellent reproducibility of the method using AuNP-MWNT/ITO electrode.

3.8. Selectivity of the method

Tryptophan often exists together with high concentration of electroactive biomolecules like uric acid and ascorbic acid in natural environments that can interfere with each other. Hence, in order to examine the selectivity of AuNP-MWNT/ITO, influence of major interferents such as uric acid, ascorbic acid and dopamine were evaluated. For this purpose square wave voltammograms of a solution having mixture of standard ascorbic acid, dopamine, uric acid and Trp were recorded at pH 7.2 using AuNP-MWNT/ITO. It was found that well separated peaks at ~50, ~150, ~300 and

~669 mV were observed corresponding to the oxidation of ascorbic acid, dopamine, uric acid and Trp, respectively. In order to further confirm the selectivity of modified sensor concentration of each interfering substance increased from 5 to 1000 fold by keeping the tryptophan concentration constant. The experimental results show that no substantial changes in peak current response of Trp were observed for entire concentration range. Therefore, it is concluded that AuNP-MWNT/ITO can be securely used for the determination of tryptophan in biological samples even in complex media.

4. Conclusions

It has been unfold that AuNP-MWNT/ITO shows an appealing voltammetric performance in comparison to bare ITO and MWNT/ITO electrodes due to its high current sensitivity and low detection limit towards tryptophan. The oxidation peak current of Trp was found to increase significantly along with a substantial shift in peak potential towards less positive potential by using AuNP-MWNT/ITO in comparison to bare ITO and MWNT/ITO electrodes. The origin of electro catalytic properties of nanotubes has been assigned to the embedded metal impurities in CNT samples and edge-plane-like defects which are present at the open ends of nanotubes [47,48]. Further, gold nanoparticles seems to again increase the electrocatalytic activity of MWNT modified electrode due to their superhydrophobicity, high specific surface area and surface enhanced Raman scattering [49]. Carboxylated MWNTs are helpful towards binding AuNPs on the MWNT layer at ITO surface. Thus, the electrocatalytic activity was found to extensively increased by using the noble combination of gold nanoparticles with carbon nanotubes. To further evaluate the performance of the AuNP-MWNT/ITO sensor towards Trp determination. A comparison of detection limit and calibration range reported in the last few years for Trp is presented in Table 2. It can be seen that the detection limit of the proposed sensor is better than several papers reported in last few years and is comparable with others. The proposed sensor has also been utilized for the electrochemical determination of Trp in human blood plasma and urine samples with reproducible results.

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